
Organic Solvent Alteration of Hydraulic Properties of Sedimentary Rocks of Low Permeability—A Review

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May 1985

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute



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PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161

NTIS Price Codes
Microfiche A01

Printed Copy

Pages	Price Codes
001-025	A02
026-050	A03
051-075	A04
076-100	A05
101-125	A06
126-150	A07
151-175	A08
176-200	A09
201-225	A010
226-250	A011
251-275	A012
276-300	A013

interaction of organic molecules with clays, including the formation of interlayer complexes and the mechanisms of expansion and contraction of clays. The latter is beyond the scope of this report.

Barshad (1952) evaluated the factors affecting interlayer expansion in montmorillonite and vermiculite. A major factor is the degree of dehydration prior to contact with the organic compound; complete dehydration resulted in lack of or reduced expansion for a number of organic solvents (hexane, benzene, butanol, glycerol, acetone). Other factors affecting expansion include the cationic form of the clay (greater expansion with smaller cation and larger valence charge on cation), the total charge on the crystal lattice (expansion increases with smaller total charge), the dielectric constant of the organic liquid (in one homologous series, as the dielectric constant increased, the expansion decreased, then increased, then decreased again), and the dipole moment of the organic liquid (expansion increased with increasing dipole moment). Brindley et al. (1969) studied the degree of expansion of Ca-montmorillonite with several organic solvents. For example, water swells montmorillonite to 19Å. Addition of as little as 1 mol% acetone results in further swelling. Addition of 20 to 60 mol% acetone results in expansion to 26.5Å. Addition of 80 to 90 mol% acetone causes shrinkage to 22Å, while pure acetone causes further shrinkage to 17.3Å. Similar results were observed with propanol, ethanol, 1,5-pentanediol, and ethylene glycol. Dioxane, by contrast, caused immediate collapse at all concentrations. Another measurement useful in determining the interactions between clays and organics is flocculation. The effectiveness of several organic compounds (including phenol, nitrophenols, quinones, phenylenediamine, gallic acids) on flocculation was shown in one study to follow the order: ^{Natural Flocculation effective} calcareous clays > noncalcareous, calcium - saturated clays > noncalcareous, sodium - saturated clays (Chang and Anderson 1968).

What is dioxane?

a clay profile should be non-leached that enhances or maintains flocculation upon exposure to "several org's"

LITERATURE REVIEW

The literature review was accomplished in three stages: (1) computerized searches of key words in several data bases (Chemical Abstracts, Biological Abstracts, NTIS, Georeferences, Water Resources Abstracts, DOE Energy Data Base); (2) review of relevant papers from the reference lists of the papers found in (1); and (3) phone calls to the authors of these papers, to additional scientists recommended by these authors, and to contacts at two petroleum companies and the National Institute of Petroleum and Energy Research (NIPER).

All three source types confirmed that very little information is available about the hydrophysical interaction of organic wastes with sedimentary rocks of low permeability. However, some information, albeit meager, is available on related subjects. Thus, this review has been divided into three areas in which information has been found. These areas were chosen to answer the following questions:

- What do we know about the effect of organic compounds on hydrophysical properties of clays?
- Is research under way concerning the interactions of organic compounds with clays and sedimentary rocks?
- What do we know about the related area of the effect of shales on inorganic transport? What other shale properties may play a role in organic interactions?

EFFECT OF ORGANIC COMPOUNDS ON HYDROPHYSICAL PROPERTIES OF CLAYS

The use of clay liners in landfills has recently led to a number of studies on the effect of organic wastes on these so-called "impermeable barriers" (i.e., impermeable to water). These studies have built on results known since at least the 1930s (e.g., Albrecht and Corey 1939, in Barshad 1952) that some clays under certain conditions expand or shrink in the presence of organic compounds. Theng (1974) has reviewed studies on the

Other studies have dealt with the hydraulic conductivity^(a) of clay to water and electrolytes. For example, Lutz and Kemper (1959) determined the permeability of four clays, each saturated with Na and Ca, to water and to electrolyte solutions. They found the following order of permeability: halloysite > Utah bentonite (granular) > Bladen clay > Wyoming bentonite. The Na clays were generally much less permeable to both water and electrolytes than were the Ca clays. In the presence of electrolyte, the Na clays showed relatively greater increases in permeability than did the Ca clays, though most of the clays were generally more permeable to electrolyte than to water. These effects are discussed in terms of the Gouy double-layer theory which is also invoked to explain the results of organic swelling experiments. Such a discussion is outside the scope of this report.

So...
Saltiness
makes
bentonite
less
predictable

the good
Ca was so
but is the
vulnerable
to leaching?

These earlier results helped to arouse suspicions that checking clay liners for permeability to water may have little bearing on their structural integrity in the presence of organic or mixed organic-inorganic wastes. Four or five groups have recently published in this or closely related areas, sometimes with conflicting results. While much of the earlier work was concerned with interlayer swelling of clays, much of this later work deals with the bulk swelling properties of clay or clay soils exposed to organic liquids.

Green et al. (1981) determined the hydraulic conductivity for three clay soils (hydrated to optimum moisture content) using water and seven organic solvents (benzene, xylene, carbon tetrachloride, trichloroethylene, acetone, methanol, and glycerol). All the clay-soils were more permeable to water than to organic solvents. This was surprising, based on two considerations: (1) $K \propto \frac{\rho}{\eta}$ where K = hydraulic conductivity or (coefficient of)

(a) Hydraulic conductivity (K) is related to intrinsic permeability (k) by the equation $K = \frac{\rho g k}{\eta}$,

where ρ is density of the fluid, η is viscosity of the fluid, and g is the acceleration due to gravity. Intrinsic permeability (length²) is a property of the soil/rock whereas hydraulic conductivity (length/time) is a combination of soil/rock and fluid properties. Because of common usage, "hydraulic conductivity" and "permeability" are used interchangeably but are distinguished from "intrinsic permeability" in the following discussion.

permeability, ρ = solvent density, and η = viscosity, and $\frac{\rho}{\eta}$ is greater for most of the organic solvents studied than for water; (2) water causes the greatest swelling of the clays which might have been expected to attenuate the flow. To resolve the problem, Green et al. (1981) attributed the low permeabilities to retardation of flow caused by preferential adsorption of the organic solvent by the clay-soil, and thus they postulated that the permeability is inversely related to the octanol-water partition coefficient (K_{ow}) and directly related to the dielectric constant [comment by Sivapullaiah and Sridharan (1984)]. Permeability also is related to the packed bulk clay density. Three exceptions to this theory were explained on the following bases. The low permeability of acetone, relative to more hydrophobic solvents, was attributed to microbial decomposition, production of CO_2 , and subsequent pore clogging. The low permeability of glycerol relative to water was attributed to its high viscosity. Perhaps the most interesting anomaly was the relatively large permeability of carbon tetrachloride (CCl_4). This was due to the tendency of CCl_4 to shrink the soil and create shrinkage channels which increased the flow of solvent. The same phenomenon can also explain the eventual breakthrough of the less polar solvents used in the experiments (i.e., benzene and xylene). Green et al. (1983) explain the expansion/shrinkage phenomenon by suggesting that polar organics can become solubilized in the soil pore water and thus cause bulk clay expansion whereas nonpolar organics cannot interact in this way and, indeed, may cause migration of water out of the clay-soil and into the bulk organic liquid (due to water's slight solubility) with subsequent shrinkage. Breakthrough of solvents caused by shrinkage has important implications for the efficacy of storage of organic solvents in clay-lined landfills.

In another series of experiments, Anderson and Brown (1981) and Brown and Anderson (1983) tested the hydraulic conductivity (permeability) of four clay-soils (noncalcareous smectite, calcareous smectite, kaolinite, illite—all with low water permeabilities) to four classes of organic solvents—basic (aniline), acidic (acetic acid), neutral